$$\beta = \phi_{C_0} + \frac{D_A}{D_C}\phi_{A_0} + \frac{D_E}{D_C}\phi_{E_0}$$

$$\delta = \frac{K_A P_0}{1+K_A P_0}\left(\frac{K_E}{K_A} - \frac{K_C}{K_A}\frac{D_E}{D_C} - \frac{K_D}{K_A}\frac{D_E}{D_D}\right)$$

with boundary conditions:

at $\eta = 0$; $\phi_A = \phi_{A_0}$ and $\phi_E = \phi_{E_0}$ and at $\eta = 1$; $\frac{d\phi_A}{d\eta} = \frac{d\phi_E}{d\eta} = 0$

Realizing that the overall reaction rate within the pore equals the rate of mass transfer across the pore mouth, the rates of reactions of A and E will respectively be proportional to

$$D_A \frac{d\phi_A}{d\eta}\bigg|_{\eta=0} \quad \text{and} \quad D_E \frac{d\phi_E}{d\eta}\bigg|_{\eta=0}$$

and, therefore, selectivity with diffusion effects can be expressed

$$S_D = \frac{D_A \dfrac{d\phi_A}{d\eta}\bigg|_{\eta=0}}{D_E \dfrac{d\phi_E}{d\eta}\bigg|_{\eta=0}}$$

The rate of reaction without diffusion effect can be obtained from equation (2) and the selectivity without diffusion can be simplified to

$$S_0 = \frac{r_A}{r_E} = \frac{k_1 K_A \left(\phi_{A_0} - \dfrac{\phi_{E_0}\phi_{C_0}}{K_1}\right)}{k_2 K_E \phi_{E_0}} \tag{6}$$

and the selectivity ratio is defined as :

$$S_R = S_D/S_0 \tag{7}$$

Effect of diffusion and adsorption on selectivity of some complex reactions correlation and case study

A THESIS

Submitted in Partial Fulfilment of the Requirements

FOR THE DEGREE OF

MASTER OF TECHNOLOGY

By

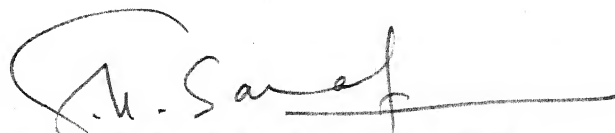**JAGDISH CHANDER GUPTA**

to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

August 1970

CERTIFICATE

It is certified that this work has been carried out under our supervision and that this has not been submitted elsewhere for a degree.

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ABSTRACT

The effect of diffusion and adsorption on the selectivity of some complex reactions is studied. All the three reaction types, namely, independent, parallel and series, are studied. The combined effect of various parameters on overall selectivity ratio of the reaction is studied. The dimensionless parameters studied are: modified Thiele parameter, ϕ_M, equilibrium constant for reversible reaction, K_1, ratio of reaction rate constants, K_2, $K_A p_0$, diffusivity ratios and adsorption equilibrium constant ratios with respect to reactant A. An attempt is made to correlate the overall selectivity ratio with individual selectivity ratios obtained by Agarwal (1) by varying only one parameter at a time. Multiple regression analysis is used to find the best correlation. Satisfactory correlations are established for independent and series reactions. No simple correlation is possible for parallel reactions.

Thiophene hydrogenolysis reaction, a series of reaction of industrial importance, is chosen for detailed study. Variations in selectivity and product distribution are presented as a function of thiophene conversion for modified Thiele parameter range of 0.2 to 2.0. As expected, the concentration of reaction intermediate is found to decrease with increase in the value of Thiele parameter for a given Thiophene conversion.

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NOMENCLATURE

a	Constant
a	Constants of the regression equation
A	Component A
A	Constant of the regression equation
A	Thiophene
B	Component B
B	Hydrogen
C	Component C
C	Butene
D	Component D
D	Diffusivity, $Cm^2/sec.$
D	Hydrogen Sulfide
E	Component E
E	Butane
k_1, k_2	Forward Reaction Velocity Constants for Reaction 1 and 2
k_1	Reverse Reaction Velocity Constant for Reaction 1
K	Adsorption Equilibrium Constant
K_1	Equilibrium Constant for Reversible Reaction
K_1	Equilibrium Constant for Irreversible Reaction
K_2	Ratio of Reaction Velocity Constants
L	Length of the Pore
p	Partial Pressure
P_0	Total Pressure Outside the Pore Mouth
r	Rate of reaction, moles/(unit volume of the catalyst pore)(sec.)
S	Cross Sectional Area of the Pore

S_0	Selectivity without diffusion effects
S_D	Selectivity with diffusion effects
S_R	Selectivity ratio, S_D/S_0
X	Individual Selectivity Ratio
X	Normalized Selectivity Ratio
Y	Overall Effect of Selectivity Ratio
Y	Overall effect of Normalized Selectivity Ratio
Z	Distance Along the Pore

Greek Letters

α	Constant of the rate equations under given conditions
β	Constant of the rate equations under given conditions
γ	Constant of the rate equations under given conditions
δ	Constant of the rate equations under given conditions
ω	Constant of the rate equations under given conditions
ξ	Constant of the rate equations under given conditions
χ	Constant of the rate equations under given conditions
ϕ	Dimensionless partial pressure, p/p_0
η	Dimensionless distance along the pore, z/L
ϕ_M	Modified Thiele Parameter
$\triangle$	Increment

Subscripts

A	Component A
B	Component B
C	Component C
D	Component D
E	Component E
n	Number
0	Condition at the pore mouth

* * *

CHAPTER I

INTRODUCTION

Many chemical reactions are carried out by contacting
a fluid and porous solid that catalyses a reaction involving
some constituent of the fluid. Essentially all surface area
of a high area catalyst is present in the interior of the
catalyst mass. Pores run through the particles in a random,
interconnecting fashion. Diffusion of gas or liquid is the
predominant mode of mass transfer within the catalyst pellet.
In some cases, bulk flow of fluid in the pores or surface
migration of adsorbed species might be significant, but
diffusion is far more important than either of these trans-
port mechanisms in most high temperature and low pressure
catalytic processes. Gaseous diffusion in commercial catalysts
is usually either in the Knudsen or transition regime, due to
small pore sizes of most high area catalysts. However in very
large pores such as occur in low area porous catalysts made
by compacting non-porous catalyst particles, bulk diffusion
may predominate.

When a reaction takes place in a porous catalyst mass,
the fluid reactants have to diffuse inside the catalyst
particle to make the effective use of the surface area available

in its pores since most of the surface area is inside the pores as pore walls. The reactants are chemisorbed and then react to form the chemisorbed product. The product molecules are then desorbed and diffuse out of the catalyst particle to the surface from which it is transferred to the bulk of the fluid. Each of these steps offer some resistance and the rate of reaction taking place in a catalyst pore depends upon the magnitude of these resistances. In the past, expressions for the rate of reaction in a catalyst pore were obtained taking into account these resistances. If all these resistances are considered together, the rate expression becomes too much involved and in many cases it is not possible to obtain the rate expression in terms of measurable quantities. For this reason generally it is assumed that out of all these steps, one of them offer maximum resistance and accordingly all others neglected. Thus the rate of reaction equals the rate of the slowest step.

As a result of pore diffusion there exists a concentration gradient inside the pore and hence reaction takes place with different rates at different positions in the catalyst pore. This affects the activity of the catalyst which is expressed in terms of effectiveness factor, defined as the actual rate of reaction divided by the rate of reaction if there is no concentration gradient due to mass transfer limitations. In complex reactions where more than one reaction is taking place, quite often, different reactions are effected

in a different way and there is change in selectivity. The term selectivity is generally defined as the rate of desired reaction divided by the rate of disappearance of the key reactant.

Agarwal (1) studied the effect of diffusion on selectivity of some complex reactions by using Langmuir-Hinshelwood type of rate expressions, which takes into account the effect of adsorption on reaction rates and the results were presented in terms of selectivity ratio as a function of modified Thiele parameter for various reaction parameters. By varying only one variable at a time while keeping all others at a constant value of unity, the effect of different parameters on the selectivity of some complex reaction was presented. However, for any actual reaction the values of most of these parameters may be greatly different from unity and as such the results can not be applied directly.

In the present work, an attempt is made to study the effect of interaction of various parameters on selectivity by arbitrarily varying the values of these parameters and to correlate these results with those obtained by Agarwal (1).

The reactions considered for detail study are:

1. Independent Reactions

$$A \rightleftharpoons B + C$$
$$E \longrightarrow D + C$$
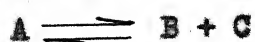
2. Parallel Reactions

$$2A \rightleftharpoons B + C$$
$$A \longrightarrow D + C$$
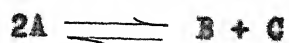
3. Series Reactions

$$A \rightleftharpoons B + C$$
$$B \longrightarrow D + C$$
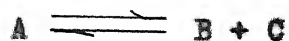
In each case the first reaction is taken as reversible to consider the effect of reversibility.

The effect of adsorption and diffusion on the selectivity of an industrially important series reaction, namely, thiophene hydrogenolysis is also studied (Appendix B) and the variation in selectivity is presented as a function of thiophene conversion for selected values of Thiele parameter.

* * *

CHAPTER II

LITERATURE REVIEW

Sherwood and Satterfield (2) in their recent book have given an excellent account of the progress made over past three decades since the pioneering work of Damkohler (3), Thiele (4) and Zeldowitch (5) in the general area of the role of diffusion in catalysis.

In catalytic reactions, the rate expressions are not simple first or second order expressions. To account for the effect of adsorption, Langmuir-Hinshelwood type of rate expressions are to be used. For the first time Chu and Hougen (6) considered the effect of adsorption on effectiveness factor by analyzing a first order irreversible reaction $A \longrightarrow B$. Roberts and Satterfield (7,8) analyzed the reaction, $A + bB \longrightarrow$ products, assuming first and second order irreversible reaction kinetics. Schneider and Mitschka (9, 10, 11, 12) and Kao and Satterfield (13) considered first order reversible reaction, $A \rightleftharpoons B$ and showed that the retardation effect (due to pore diffusion) is more for reversible reactions that for irreversible reactions.

For complex reactions the effect of pore diffusion selectivity was studied by Wheeler (14) who designated ·

different types of selectivity, since each is affected
quite differently by the pore diffusion. Selectivity
for independent reactions has been studied by Wheeler (14);
for parallel reactions by Ostergaard (15) and Powloski (16);
and for series reactions by Carberry (17),Weiz (5) and
Wheeler (14). All of them have considered simple first
or higher order reaction kinetics.

Agarwal (1) has studied the effect of diffusion and
adsorption on selectivity of some complex reactions in a
cylindrical pore without radial gradients using Langmuir-
Hinshelwood type of rate expressions to take care of adsorption
effects. He assumed that the surface reaction controls the
rate of reaction. In this study the effect of pressure
gradient, changes in the diffusivities and adsorption equi-
librium constants within the pore were neglected. Diffusion
with chemical reaction gives rise to a set of non-linear
differential equations of the boundary value type whose initial
conditions are missing. The solution was achieved by quasi-
linearization (18) and invariant imbedding techniques (19).

* * *

CHAPTER III

MATHEMATICAL FORMULATION OF THE PROBLEM
AND THE SOLUTION TECHNIQUES

This chapter presents the important results of the mathematical developments carried out by Agarwal (1) for the sake of continuity and clarity of presentation of the work done by the author.

A. Independent Reactions:

When two reactions with different reactants are taking place on a catalyst, the reactions are called independent reactions. The reaction scheme considered for detailed study is same as that of Agarwal (1) and is given below:

$$A \xrightleftharpoons[k_1']{k_1} B + C \qquad (1)$$

$$E \xrightarrow{k_2} D + C$$
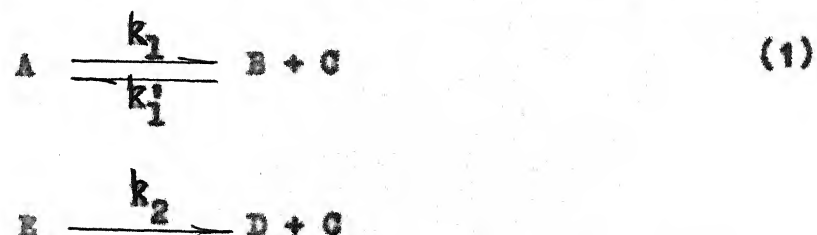
If single site mechanism is assumed for both the reactions, where component C is reacting in the gas phase and surface reaction controls the rate of reaction, the rate expressions

for components A and E can be written as

$$-r_A = \frac{k_1 \, K_A \left(p_A - \frac{p_B p_C}{K}\right)}{\left(1 + \sum_i K_i \, p_i\right)}$$

(2)

$$-r_E = \frac{k_2 \, K_E \, p_E}{\left(1 + \sum_i K_i p_i\right)}$$

where r_A and r_E are the rate of formation of component A and E per unit pore volume. k_1, k_1' and k_2 are the reaction rate constants for the adsorbed species in the direction indicated in equation (1), K_i is the adsorption equilibrium constant for component i, p_i is the partial pressure of component i, K is the equilibrium constant for the first reaction and subscript i stands for all components present in the reaction mixture viz., A, B, C, D and E. The rate of reaction of other components can be obtained from simple stoichiometry

$$r_B = - r_A$$
$$r_D = - r_E$$
$$r_C = r_B + r_D$$

(3)

with simultaneous diffusion and reaction within the pore, at steady state, the mass balance for any component

$$D_i \, \frac{d^2 c_i}{dz^2} = -r_i$$

(4)

Without going through the details of mathematical development which are explained by Agarwal (1), only the final form of differential equations with dimensionless variables are reproduced below:

$$\frac{d^2\phi_A}{d\eta^2} = \frac{\phi_M^2\left[\phi_A - (\alpha - \frac{D_A}{D_B}\phi_A)(\beta - \frac{D_A}{D_C}\phi_A - \frac{D_E}{D_C}\phi_E)/K_1\right]}{\omega + \gamma\,\phi_A + \delta\,\phi_E} \tag{5a}$$

$$\frac{d^2\phi_E}{d\eta^2} = \phi_M^2\,\frac{1}{K_2}\,\frac{D_A}{D_E}\,\frac{\phi_E}{(\omega + \gamma\,\phi_A + \delta\,\phi_E)} \tag{5b}$$

where $\phi = p/p_0$

$\eta = z/L$

$K_1 = K/p_0$

$\phi_M = L\sqrt{\dfrac{K_1\,K_A\,RT}{D_A(1 + K_A\,p_0)}}$

$\omega = \dfrac{1}{1 + K_A p_0} + \dfrac{K_A\,p_0}{1 + K_A p_0}\left[\alpha\dfrac{K_B}{K_A} + \beta\dfrac{K_C}{K_A} + \right.$

$\left. \dfrac{K_D}{K_A}(\phi_{D_0} + \dfrac{D_E}{D_D}\phi_{E_0})\right]$

$\alpha = \phi_{B_0} + \dfrac{D_A}{D_B}\phi_{A_0}$

$\gamma = \dfrac{K_A\,p_0}{1 + K_A p_0}\left(1 - \dfrac{K_B}{K_A}\,\dfrac{D_A}{D_B} - \dfrac{K_C}{K_A}\,\dfrac{D_A}{D_C}\right)$

To get selectivity ratio, the values of $\left.\dfrac{d\,\phi_A}{d\eta}\right|_{\eta=0}$ and $\left.\dfrac{d\,\phi_E}{d\eta}\right|_{\eta=0}$ are to be obtained which are nothing but the missing initial conditions of the equations(5a) and (5b). The special case studied assumes that the concentration of products at pore mouth is zero and the two reactants are present in equal proportion, that is $\phi_{B_0} = \phi_{C_0} = \phi_{D_0} = 0$ and $\phi_{A_0} = \phi_{E_0} = 0.5$.

B. Parallel Reactions:

When two or more reactions with same reactants are taking place on a catalyst surface the reactions are called parallel reactions. The reaction scheme considered for study is same as that of Agarwal(1) and is given below:

$$2A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} B + C \tag{8}$$

$$A \xrightarrow{k_1} D + C$$

If dual site mechanism for the first reaction and single site mechanism for the second reaction are assumed, the rate expressions for B and D can be expressed as follows:

$$r_B = \frac{k_1\, K_A^2\, \left(p_A^2 - \dfrac{p_B\, p_C}{K_1}\right)}{\left(1 + \sum_i K_i p_i\right)^2} \tag{9}$$

$$r_D = \frac{k_2\, K_A\, p_A}{\left(1 + \sum_i K_i p_i\right)}$$

The rate of reaction of other components can be obtained from simple stoichiometry

$$-r_A = 2 \; r_B + r_D$$

$$r_C = r_B + r_D \tag{10}$$

Without going through the details, only the final form of differential equation is given below:

$$\frac{d^2\phi_B}{d\eta^2} = - \frac{\phi_M^2 \left(\frac{D_A}{D_B}\right) \frac{K_A p_o}{1+K_A p_o} \left[(\alpha_1 - 2\frac{D_B}{D_A}\phi_B - \frac{D_D}{D_A})^2 - \frac{\phi_B}{K_1}(\beta_1 + \frac{D_B}{D_C}\phi_B + \frac{D_D}{D_C} \right.}{(\omega_1 + \gamma_1 \phi_B + \delta_1 \phi_D)^2}$$

$$\frac{d^2\phi_D}{d\eta^2} = - \frac{\phi_M^2 \frac{1}{2} \frac{D_A}{D_D}(1 - \frac{2D_B}{D_A}\phi_B - \frac{D_D}{D_A}\phi_D)}{(\omega_1 + \gamma_1 \phi_B + \delta_1 \phi_D)} \tag{11}$$

where

$$\omega_1 = \frac{1}{1+K_A p_o} + \frac{K_A p_o}{1+K_A p_o}(\alpha_1 + \frac{K_C}{K_A}\beta_1)$$

$$\gamma_1 = \frac{K_A p_o}{1+K_A p_o}(\frac{K_B}{K_A} - \frac{2D_B}{D_A} + \frac{K_C}{K_A} \frac{D_B}{D_C})$$

$$\beta_1 = \phi_{C_o} - \frac{D_B}{D_C}\phi_{B_o} - \frac{D_D}{D_C}\phi_{D_o}$$

$$\delta_1 = \frac{K_A p_o}{1+K_A p_o}(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{K_C}{K_A} \frac{D_D}{D_C})$$

$$\alpha_1 = \phi_{A_o} + \frac{2D_B}{D_A}\phi_{B_o} + \frac{D_D}{D_A}\phi_{D_o}$$

With boundary conditions:

$$\text{at } \eta = 0; \quad \phi_B = \phi_{B_o} \quad \text{and} \quad \phi_D = \phi_{D_o}$$

$$\text{and at } \eta = 1 \quad \frac{d\phi_B}{d\eta} = \frac{d\phi_D}{d\eta} = 0$$

The selectivity with diffusion effects is defined as

$$S_D = \frac{\text{Rate of formation of B within the pore}}{\text{Rate of disappearance of A with in the pore}}$$

$$= \frac{\dfrac{D_B}{D_A} \left. \dfrac{d\phi_B}{d\eta} \right|_{\eta = 0}}{2 \dfrac{D_B}{D_A} \left. \dfrac{d\phi_B}{d\eta} \right|_{\eta = 0} + \dfrac{D_D}{D_A} \left. \dfrac{d\phi_D}{d\eta} \right|_{\eta = 0}}$$

The rate of reaction without diffusion effects can be obtained by proper substitution in rate equation (9) to give selectivity without diffusion effects as

$$S_O = \frac{r_{B_o}}{2r_{B_o} + r_{D_o}} \tag{12}$$

The selectivity ratio is again defined as in equation (7). The special case studied assumes that the concentration of products at pore mouth is zero and only reactant A is present that is,

$$\phi_{B_o} = \phi_{C_o} = \phi_{D_o} = 0 \quad \text{and} \quad \phi_{A_o} = 1.$$

C. Series Reactions

When the product of a reaction further reacts to form a new product (D), the reactions are called series reactions. The reaction scheme considered for detailed study is same as that of Agarwal (1) and given below:

$$A \; \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \; B + C$$

$$B \; \overset{k_2}{\longrightarrow} \; D + C \tag{13}$$
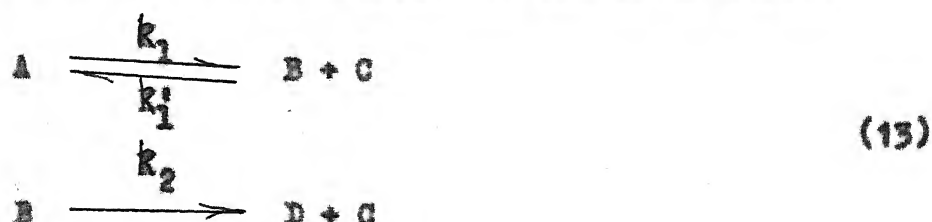
If single site mechanism is assumed for both the reactions with C reacting in the gas phase and also if surface reaction controls the rate of reaction, the following rate expressions can be obtained for the component B and D:

$$r_B = \frac{k_1 \, K_A \left(p_A - \dfrac{p_B \, p_C}{K} - \dfrac{p_B}{K_2} \right)}{\left(1 + \sum\limits_i K_i \, p_i \right)}$$

$$r_D = \frac{k_2 \, K_B \, p_B}{\left(1 + \sum\limits_i K_i \, p_i \right)} \tag{14}$$

where $\quad K = \dfrac{k_1 \, K_A}{k_1' \, K_B} \quad$ and

$$K_2 = k_1 \, K_A / k_2 \, K_B$$

The rate of other components can be obtained from simple stoichiometry

$$-r_A = r_B + r_D$$

$$r_C = -r_A + r_D \tag{15}$$

The final expressions after proper substitutions and simpli-
fications are as follows:

$$\frac{d^2\phi_B}{d\eta^2} = - \frac{\phi_M^2 \frac{D_A}{D_B}\left[\alpha_2 - (\frac{D_B}{D_A} + \frac{\beta_2}{K_1} + \frac{1}{K_2})\phi_B - \frac{D_D}{D_A}\phi_D - \frac{\phi_B}{K_1}(\frac{D_B}{D_C}\phi_B + \frac{2D_D}{D_C}\phi_D)\right]}{(\omega_2 + \gamma_2\phi_B + \delta_2\phi_D)}$$

$$\frac{d^2\phi_D}{d\eta^2} = -\phi_M^2 \frac{1}{K_2}\frac{D_A}{D_D}\frac{\phi_B}{(\omega_2 + \gamma_2\phi_B + \delta_2\phi_D)} \tag{16}$$

where

$$\omega_2 = \frac{1}{1+K_A P_0} + \frac{K_A P_0}{1+K_A P_0}(\alpha_2 + \frac{K_C}{K_A}\beta_2)$$

$$\gamma_2 = \frac{K_A P_0}{1+K_A P_0}(\frac{K_B}{K_A} - \frac{D_B}{D_A} + \frac{K_C}{K_A}\frac{D_B}{D_C})$$

$$\delta_2 = \frac{K_A P_0}{1+K_A P_0}(\frac{K_D}{K_A} - \frac{D_D}{D_A} + \frac{2K_C}{K_A}\frac{D_D}{D_C})$$

$$\alpha_2 = \phi_{A_0} + \frac{D_B}{D_A}\phi_{B_0} + \frac{D_D}{D_A}\phi_{D_0}$$

$$\beta_2 = \phi_{C_0} - \frac{D_B}{D_C}\phi_{B_0} - \frac{2D_D}{D_A}\phi_{D_0}$$

The rate of reaction without diffusion effects can be obtained
by proper substitution in rate equation (14) to give selectivity
without diffusion effects as

$$S_0' = \frac{r_B}{r_B + r_D} \tag{17}$$

and the selectivity ratio will again be defined by equation (7).

The special case studied assumes $\phi_{B_o} = \phi_{C_o} = \phi_{D_o} = 0$ and $\phi_{Ao} = 1$ as in the case of parallel reaction scheme.

D. Solution of a System of Non Linear Boundary Value Problems:

Agarwal (1) used the following two different techniques for the determination of initial missing conditions for a system of non linear boundary value problem.

1. Quasi-Linearization Method
2. Invariant Imbedding Technique

The Quasi-Linearization technique gives reliable results for the entire Thiele parameters range studied, where as the invariant imbedding technique was found to be particularly useful for low Thiele parameter data. The advantage of invariant imbedding technique is that it takes much less time in comparison to that taken by quasi-linearization technique.

In the present study more general programme for each of the two techniques was developed for all different types of reactions schemes mentioned earlier. It was thus possible to study the effect on selectivity of these reaction systems for arbitrarily chosen values of different variable defining the system. The restriction of varying only one variable at a time was removed. These results were used to establish some reasonable correlation to predict the selectivity ratio for a general system where most or all of the variables have

values different from unity, from the selectivity ratio data of Agarwal (1) where only one variable was varied at a time while keeping the value of all other variables at unity.

* * *

CHAPTER IV

CORRELATION OF DATA

A. Analysis of the Interaction of Various Parameters:

In this chapter, the interaction of various reaction parameters and the consequent influence on over all selectivity of the reaction for a given value of modified Thiele parameter is analyzed. Agarwal (1) has presented his results in terms of selectivity ratio, as a function of modified Thiele parameter for various reaction parameters, by varying only one variable at a time while keeping all others at a constant value of unity. To estimate the overall effect for a system with arbitrarily assigned values of different parameters from the one parameter data of Agarwal (1), the most logical correlation may be to assume that the combined effect on overall selectivity ratio is obtained by taking the product of individual selectivity ratios obtained by varying single parameter. To fit the data each of the individual selectivity ratio are raised to a constant power that is

$$Y = A_o (X_1)^{a_1} (X_2)^{a_2} - - - (X_n)^{a_n} \qquad (18)$$

and the values of these constants, a_o to a_n, are to be determined using multiple regression method. The correlation can be done in one of the following two ways:

(i) Y represents combined and X_1 to X_n represent individual selectivity ratios as such

(ii) Y represents combined and X_1 to X_n represent individual selectivity ratios each after dividing by the selectivity ratio value when all parameters except Thiele parameter (the value of which is taken as that of the actual system), are taken as unity.

The equation 18 can be written in algebraic form which is amenable to regression analysis simply by taking the logrithm to give

$$\ln Y = A_0 + a_1 \ln X_1 + a_2 \ln X_2 \ldots\ldots + a_n \ln X_n$$

(19)

The latter method was found to be more promising and was, therefore, chosen for detailed study. A careful study of the results of Agrawal (1) indicated that not all variable parameters have significant influence on selectivity ratio value. It was therefore found desirable to include only those variables, which were observed to influence the selectivity ratio significantly.

B. Multiple Regression Analysis:

Regression analysis (22) is designed to examine the relationship between Y to a variable X. Here X is independent variable and is assumed to have no error associated with it. This variable is selected arbitrarily for the purpose of studying Y. Y is a dependent variable and the relationship between X and Y

is such that

$$Y_i = A + B X_i + \epsilon_i$$

where A and B are parameters of the population and ϵ_i is a random variable (deviation from a population or true line of regression) with mean zero while the X values are selected by the researcher.

The model of interest is

$$y = a_0 + a_1 x_1 + a_2 x_2 + \ldots\ldots + a_n x_n \qquad (20)$$

where $y = \ln Y$, $a_0 = \ln A_0$, $x_i = \ln X_i$, $i = 1$ to n.

For finding the constants, least square method assures us that sum of the squares of the vertical deviations from the fitted line will be less than the sum of the squares of the vertical deviations from any other line, no matter how computed. For finding a's we minimize the sum of squares of deviations,

$$\sum \left[y - (a_0 + a_1 x_1 + a_2 x_2 + \ldots\ldots + a_n x_n) \right]^2$$

differentiating with respect to a_1 and equating to zero we get first equation and when differentiated with respect to $a_2, \ldots.. a_n$ the succeeding equations are obtained. These are called normal euations. For the validity of the final results, the resulting residual sum of squares should be zero that is $\sum (y - \bar{y}_x) = 0$ where y is the true value and $\bar{y}_x$ is the computed value, that is, regression sum of squares equals total sum of squares. This provides a measure of the degree to which the dependent variable is influenced by the n independent variables.

CHAPTER V

RESULTS AND DISCUSSIONS

The following dimensionless variables are studied for their interaction on selectivity ratio

- Modified Thiele parameter, ϕ_M

- Reaction equilibrium constant, K_1

- Ratio of reaction velocity constants, K_2

- $K_A P_0$

- Ratio of diffusivities, $\dfrac{D_B}{D_A}$, $\dfrac{D_C}{D_A}$, $\dfrac{D_D}{D_A}$, $\dfrac{D_E}{D_A}$

- Ratio of adsorption equilibrium constants, $\dfrac{K_B}{K_A}$, $\dfrac{K_C}{K_A}$, $\dfrac{K_D}{K_A}$, $\dfrac{K_E}{K_A}$

that is, the no. of variables studied, excluding modified Thiele parameter are eleven for independent reactions and nine for parallel as well as series reactions. The range of the values of each of the variables is given in the following Table 1

TABLE 1: Range of the Values of the Variables Studied

Variable	Range		
ϕ_M	0.4	-	4.0
K_1	0.1	-	100
K_2	0.1	-	10
$K_A P_0$	0.01	-	100
D_B/D_A, D_C/D_A, D_D/D_A, D_E/D_A	0.25	-	4.0
K_B/K_A, K_E/K_A	0.25	-	4.0
K_C/K_A, K_D/K_A	0.0	-	4.0

Modified Thiele parameter, $\emptyset_M$ is defined as $L\sqrt{\dfrac{K_1\,K_A\,RT}{D_A\,(1+K_A P_o)}}$

A. INDEPENDENT REACTIONS:

Table 2 shows the maximum range of variation of normalized selectivity ratio for all the eleven dimensionless parameters and, in general, corresponds to the variation at the highest value of Thiele parameter as reported by Agarwal (1). 'Appreciable' in remark column of the Table 2 indicates that this variable has significant effect and is included for regression analysis. The variables with "negligible" effect are not used in regression analysis and the value of a_i for these variables is assumed to be unity.

TABLE 2: Maximum Variations in Normalized Selectivity Ratio

Variable	Normalized*maximum selectivity ratio variation.	Remarks
K_1	0.625 — 1.21	Appreciable
K_2	0.345 - 2.94	Apprecible
$K_A P_o$	0.99 - 1.005	Negligible
D_B/D_A	0.79 - 1.15	Appreciable
D_C/D_A	0.81 - 1.14	Appreciable
D_D/D_A	0.99 - 1.01	Negligible
D_E/D_A	0.5 - 2.11	Appreciable
K_B/K_A	0.99 - 1.02	Negligible
K_C/K_A	0.98 - 1.04	Negligible
K_D/K_A	0.98 - 1.03	Negligible
K_E/K_A	0.98 - 1.02	Negligible

*All the selectivity ratio values are divided by the selectivity ratio value when all the variable parameters, except Thiele parameter, are at unity.

Table 2 indicates that variable parameters $K_A p_o$, D_D/D_A , K_B /K_A, K_C/K_A K_D /K_A and K_E /K_A have very small influence on the selectivity ratio and only the following parameters need detailed study for their influence:

$$K_1, \quad K_2, \quad D_B/D_A, \quad D_C/D_A \text{ and } D_E/D_A.$$

Using the generalized programme, Appendix A, the overall selectivity ratio was calculated for arbitrarily chosen values of parameters K_1, K_2, D_B/D_A, D_C/D_A and D_E/D_A at modified Thiele parameter values of 0.4, 0.7, 1, 2 and 4. The values of individual selectivity ratio corresponding to the single parameter variation only at the same Thiele parameter were obtained from the studies of Agrawal(1). Taking a sample size of 164 data points selected randomly, the regression analysis resulted in the best fit with the following values of the constants in equation 18 page 18.

$$A_o = 0.93$$
$$a_1 = 1.42$$
$$a_2 = 0.95$$
$$a_3 = 1.17$$
$$a_4 = 1.16$$
$$a_5 = 1.06$$

where subscript 1,2,3,4 and 5 refer respectively to variable parameters K_1, K_2, D_B/D_A, D_C/D_A and D_E/D_A. As indicated earlier all other a_i corresponding to the remaining variables are taken as unity since their influence on selectivity ratio is small.

The error distribution analysis for 164 random observations taken at the Thiele parameter range of 0.4 to 4 is given in Table 3.

This error distribution shows that nearly eightysix percent of the observations are within thirty percent error of the true calculated value of the overall selectivity ratio. The variation in the calculated value of overall selectivity ratio was observed in the range of 0.3 to 3.6 for the data samples investigated

B. SERIES REACTIONS

Table 4 shows the maximum range of the variation of normalized selectivity ratio for all the nine dimensionless parameters and, in general, corresponds to the variation at the highest value of Thiele parameter as reported by Agarwal (1). 'Appreciable' in remark column of the Table 4 indicate that this variable has significant effect and is included for regression analysis. The variables with "negligible" effect are not used in regression analysis and the value of a_i for these variables is assumed to be unity.

Table 4 indicates that variable parameters D_D/D_A and K_D/K_A have very small influence on the selectivity ratio and only the following parameters need detailed study for their relative influence

K_1, K_2, $K_A P_o'$, D_B/D_A, D_C/D_A, K_B/K_A and K_C/K_A. Using the generalized program, Appendix A, the overall selectivity ratio was calculated for arbitrarily chosen values of parameters K_1, K_2, $K_A P_o'$

TABLE 3: <u>DISTRIBUTION ANALYSIS FOR INDEPENDENT REACTIONS</u>

Observations within	For 27 observations at $\phi_M=.4$	For 37 observations at			For 26 observations at $\phi_M=4$	For 164 observations at $\phi_M=-.4, .7, 1,2,\& 4$
		$\phi_M=.7$	$\phi_M=1.0$	$\phi_M=2$		
five percent error	11	11	6	7	8	43
five to ten percent error	7	8	7	2	6	30
ten to twenty percent error	4	5	11	13	9	42
twenty to thirty percent error	3	7	5	8	2	25
thirty to forty percent error	1	2	2	2	–	7
forty to fifty percent error	–	1	2	3	1	7
Observations with greater than fifty percent error	1	3	4	2	–	10

TABLE 4: Maximum Variations in Normalized Selectivity
Ratio

Variable	Normalized maximum selectivity ratio variation			Remarks
K_1	0.98	–	1.17	Appreciable
K_2	0.45	–	1.38	Appreciable
K_A/P_o	0.93	–	1.05	Appreciable
D_B/D_A	0.69	–	1.29	Appreciable
D_C/D_A	0.93	–	1.13	Appreciable
D_D/D_A	0.98	–	1.04	Negligible
K_B/K_A	0.95	–	1.05	Appreciable
K_C/K_A	0.93	–	1.12	Appreciable
K_D/K_A	0.98	–	1.03	Negligible

D_B/D_A, D_C/D_A, K_B/K_A and K_C/K_A at modified Thiele parameter values
of 0.4, 0.7, 1, and 2. The values of individual selectivity
ratio corresponding to the single parameter variation only at
the same Thiele parameter are obtained from the studies of
Agrawal (1). Taking a sample size of 71 data points selected
randomly, the regression analysis resulted in the best fit
with the following values of the constants in equation 18 page 18

$$A_o = 0.99$$

$$a_1 = -0.14$$

$$a_2 = 1.13$$

$$a_3 = 0.19$$

$$a_4 = 1.02$$

$$a_5 = 2.38$$
$$a_6 = 2.01$$
$$a_7 = 1.86$$

where subscript 1,2, ---- - and 7 refer respectively to variable parameters K_1, K_2, $K_A P_0$, D_B/D_A, D_C/D_A, K_B/K_A, K_C/K_A. As indicated earlier all other a_i corresponding to the remaining variables are taken as unity since their influence on selectivity ratio is small.

The error distribution analysis for 71 random observations at the Thiele parameter range of 0.4 to 2 is given in Table 5

TABLE 5: <u>Distribution Analysis for Series Reactions</u>

Error Distribution within	For 19 observations at ϕ_M=.4	For 17 observations		For 18 observations at ϕ_M= 2	For 71 observations at ϕ_M=.4 .7,1 & 2
		at ϕ_M=.7	at ϕ_M= 1		
five percent error	9	5	3	6	23
five to ten percent error	8	6	6	10	30
ten to twenty percent error	2	5	8	2	17
twenty to thirty percent error	-	1	-	-	1

The error distribution shows that nearly ninety nine percent of the observations are within twenty percent error of the true calculated value of the overall selectivity ratio. The variation in the calculated value of overall selectivity ratio was observed in the range of 0.4 to 1.45 for data samples investigated.

C. PARALLEL REACTIONS

The Table 6 shows the maximum range of the variation of normalized selectivity ratio for all the nine dimensionless parameters, and, in general corresponds to the variation at the highest value of Thiele parameter as reported by Agrawal (1). 'Appreciable' in remark column of the Table 6 indicates that this variable has significant effect and is included for regression analysis. The variables with 'negligible' effect are not used in regression analysis and the value of a_i for these variables is assumed to be unity.

TABLE 6: Maximum Variations in Normalized Selectivity Ratio

Variable	Normalized maximum selectivity ratio variation			Remarks
K_1	0.785	–	1.07	Appreciable
K_2	0.723	–	1.485	Appreciable
$K_A P_o$	0.91	–	1.085	Appreciable
D_B/D_A	0.89	–	1.05	Appreciable
D_C/D_A	0.91	–	1.07	Appreciable
D_D/D_A	0.98	–	1.05	At a lower Thiele parameter, Appreciable
K_B/K_A	0.995	–	1.00	Negligible
K_C/K_A	0.97	–	1.05	At a lower Thiele parameter, Appreciabl
K_D/K_A	0.975	–	1.05	–do–

It is observed from the Table 6 that variation of the ratio of selectivity ratio is almost negligible for K_B/K_A. Though the

variations of D_D/D_A, K_C/K_A and K_D/K_A are also very small at
the highest available Thiele parameter but the variations at
lower Thiele parameter are appreciable, these are, therefore,
taken into the analysis. In this case since the combined
selectivity ratio was found to vary over a very wide range
of 0.04 to 12.5, it was not possible to use the same constants
over the entire range of Thiele parameter, so as to obtain
a generalized expression to calculate combined selectivity
ratio with reasonable accuracy. Using the multiple regression
analysis separately for each Thiele parameter region, that is
low ($\phi_M = 0.4$), moderate ($\phi_M = 0.7$ and 1) and high ($\phi_M = 2$ and 4)
the following values of constants (Table 7) were obtained. The
results are tabulated below for all the three cases in Table 7.

TABLE 7: Values of Constants for Parallel Reactions

Parameter	Constant	Value of Constant for Thiele Parameter Value of		
		$\phi_M = 0.4$	$\phi_M = 0.7$ & 1	$\phi_M = 2$ and 4
	A_0	1.11	2.85	0.97
K_1	a_1	38.7	-3.33	0.66
K_2	a_2	-0.67	1.4	0.87
$K_A P_0$	a_3	-4.15	0.27	0.82
D_B/D_A	a_4	131.5	12.35	-17.7
D_C/D_A	a_5	20.0	-25.37	4.38
D_D/D_A	a_6	62.7	57.5	64.34
K_C/K_A	a_7	9.02	3.84	-9.22
K_D/K_A	a_8	4.37	0.04	25.92

In view of the large values of constants as determined
by the regression analysis, the usefulness of equation 18 page
18 to predict the combined selectivity ratio is open to serious
doubts. The error distribution analysis for three ranges of
Thiele parameter is given in Table 8.

Using these values of constants, even though seventy five
percent 'data points'of low Thiele parameter range, ninety percent
data points of moderate Thiele parameter range and ninety five
percent data points of high Thiele parameter range lie within
thirty percent error, the applicability of equation 18, page 18,
to predict overall selectivity ratio value is not recommended
because of the large values of these constants.

TABLE 8: Error Distribution Analysis for Parallel Reactions

Observations within	For 53 observations at ϕ_M=.7	For 39 observations at ϕ_M=1	For 92 observations at ϕ_M=.7 and 1	For 29 observations at ϕ_M=2	For 10 observations at ϕ_M=4	For 39 observations at ϕ_M=2 and 4	For 18 observations at ϕ_M = 0.4
five percent error	7	2	9	12	4	16	3
five to ten percent error	12	2	14	6	3	9	5
ten to twenty percent error	25	13	38	8	1	9	4
twenty to thirty percent error	5	16	21	3	–	3	1
thirty to forty percent error	4	6	10	–	–	–	2
forty to fifty percent error	–	–	–	–	–	–	1
observations with greater than fifty percent error	–	–	–	–	2	2	2

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions:

1. All the dimensionless parameters do not effect the reaction selectivity to same degree. The dimensionless parameters having significant influence are:

a. Independent Reactions: reaction equilibrium constant K_1, ratio of reaction rate constant K_2, and diffusivity ratios D_B/D_A, D_C/D_A and D_E/D_A .

b. Series Reaction: K_1, K_2, $K_A P_o$, D_B/D_A, D_C/D_A, and adsorption equilibrium constant ratios K_B/K_A and K_C/K_A.

c. Parallel Reaction: All parameters except K_B/K_A.

2. Satisfactory correlations to estimate the overall selectivity ratio from individual selectivity ratios (obtained by varying at a time only one parameter) are found for independent and series reactions. For series reactions ninety nine percent of the seventy one data points are found to lie within twenty percent of the true calculated value. For independent reactions eighty five percent of the 164 data points are found to lie within thirty percent.

3. No single correlation is found to be applicable for parallel reactions in the entire range of Thiele parameter studied. Furthermore some of the computed values of the constants for use in correlations are very large and unrealistic.

4. The study of Thiophene hydrogenolysis showed that the selectivity and product distribution was significantly influenced by thiophene conversion and Thiele parameter. Increase in the value of Thiele parameter reduced the concentration of reaction intermediate. Increase in conversion also showed a similar effect on product distribution.

B. Recommendations:

1. Correlations to predict overall selectivity from individual selectivity, eventhough useful to estimate the relative effect of various parameters on overall selectivity, may not provide the complete answer, and individual reaction scheme may be studied separately using the generalized programme with actual values of various reaction parameter.

2. The technique developed is of great practical value and the application can be extended to other industrially important reactions.

* * *

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```
$JOB    CGG094,TIME008,PAGES030,NAME  J.C.GUPTA
$IBJOB
$IBFTC
        DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),G(1000),
       1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000),B(50)
C       GENERAL   PROGRAMME   FOR INDEPENDENT         REACTIONS  USING
C           QUASI  LINEARIZATION      TECHNIQUE
C     FOR  EFFECT  OF  DIFFUSION  AND  ADSORPTION  ON  SELECTIVITY
C             OF    SOME   COMPLEX      REACTIONS
 130    FORMAT(//2X,120(1H-))
        CALL  FLOV(10000)
        C=.1E+07
 11     READ1,A,(B(I),I=1,11)
 1      FORMAT(12F6.2)
        ITERAT=0.
        XO=0.
        YO=0.
        DO 2 I=1,1000
        X(I)=0.001
 2      Y(I)=0.001
        BB95=B(9)/B(5)
        BB84=B(8)/B(4)
        BB97=B(9)/B(7)
        BB133=1./(1.+B(3))
        BB76=B(7)/B(6)
        BB74=B(7)/B(4)
        BB27=1./(B(7)*B(2))
        BB313=B(3)/(1.+B(3))
        BB45=1./(B(4)*B(5))
        BB745=(B(7))/(B(4)*B(5))
        BB75=B(7)/B(5)
        BB5=1./B(5)
        BB145=B(1)*B(4)*B(5)
        BB17=1.+B(7)
        BB4=1./B(4)
        PRINT  130
 7      ITERAT=ITERAT+1
        CALL  FLUN(30000)
        DO  3  I=1,999
        R(I)=(A*A/BB145)*(BB145*X(I)-(0.5-X(I))*(0.5*BB17-X(I)-Y(I)*B(7)))
        S(I)=
       1BB133+BB313*.5*(BB84+BB17*BB95+BB76*B(10))+BB313*((1.-BB84-BB95)*
       2X(I)+Y(I)*(B(11)-B(9)*BB75-B(10)*BB76))
        H(I)=-(2.*C-(R(I)*BB313*(1.-BB84-BB95)/S(I)**2)+(A*A/BB145)*
```

```
     1(BB145+0.5+0.5*BB17-2.*X(1)-D(7)*Y(I))/S(I))
      E(I)=-(2.*C-(A*A*BB27*Y(I)*BB313*(D(11)-B(9)+BB75-B(10)*BB76))/(S
     1(I)*S(I))+(A*A*BB27)/S(I))
      V(I)=(R(I)/S(I))+X(I)*(H(I)-2.*C)
      W(I)=(A*A*BB27*Y(I)/S(I))+Y(I)*(E(I)+2.*C)
3     CONTINUE
      W(1)=W(1)-.5*C
      V(1)=V(1)-0.5*C
      H(999)=H(999)+C
      E(999)=E(999)+C
      P(1)=H(1)
      Q(1)=C/P(1)
      G(1)=V(1)/P(1)
      PP(1)=E(1)
      QQ(1)=C/PP(1)
      GG(1)=W(1)/PP(I)
      DO 4 I=2,999
      P(I)=H(I)-C*Q(I-1)
      Q(I)=C/P(I)
      G(I)=(V(I)-C*G(I-1))/P(I)
      PP(I)=E(I)-C*QQ(I-1)
      QQ(I)=C/PP(I)
      GG(I)=(W(I)-C*GG(I-1))/PP(I)
4     CONTINUE
      X(999)=G(999)
      Y(999)=GG(999)
      DO 5 I=1,998
      M=999-I
      X(M)=G(M)-Q(M)*X(M+1)
5     Y(M)=GG(M)-QQ(M)*Y(M+1)
      X1=(X(1)-.5)*1000.
      Y1=(Y(1)-.5)*1000.
      IF(ABS(XO-X1)-.001)15,15,16
15    IF(ABS(YO-Y1)-.001)17,17,16
16    XO=X1
      YO=Y1
      IF(ITERAT.GT.10) GO TO 11
      GO  TO  7
17    AB=(X1*BB27)/Y1
      PRINT8,A,(B(I),I=1,11),X1,Y1,AB
8     FORMAT(12F6.2,8X,3E16.8)
      GO  TO  11
111   STOP
      END
SENTRY
```

```
JOB    CGG094,TIME008,PAGES020,NAME  J.C.GUPTA
ILJOB
BFTC
     DIMENSION X(1000),Y(1000),H(1000),E(1000),P(1000),Q(1000),G(1000),
    1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000),B(50)
     GENERAL  PROGRAMME  FOR SERIES  REACTIONS  USING
          QUASI  LINEARIZATION   TECHNIQUE
     FOR EFFECT  OF  DIFFUSION  AND  ADSORPTION  ON  SELECTIVITY
          OF  SOME  COMPLEX  REACTIONS
 30  FORMAT(/2X,120(1H-))
     C=.1E+07
     READ 1,A,(B(I),I=1,9)
     FORMAT(10F7.2)
     ITERAT=0
     XO=0.
     YO=0.
     DO 2 I=1,1000
     X(I)=0.001
     Y(I)=.001
     PRINT130
     ITERAT=ITERAT+1
     SS=   B(8)*B(4)/B(5)
     FAC=B(3)/(1.+B(3))
     DO 3 I=1,999
     R(I)=(-A*A/B(4))*(1.-(B(4)+1./B(2))*X(I)-B(6)*Y(I)-(X(I)*B(4)/B(5)
    1+2.*B(6)*Y(I)/B(5))*X(I)/B(1))
     S(I)=1.+FAC*((B(7)-B(4)+SS          )*X(I)+(B(9)-B(6)+(2.*
    1B(8)*B(6))/B(5))*Y(I))
     H(I)=-(2.*C+ (-A*A/B(4))*(  -(B(4)+1./B(2))-(2.*X(I)*B(4)/B(5)+2.*
    1B
    2(6)*Y(I)/B(5))*1./B(1)) /S(I)-(R(I)*FAC*(B(7)-B(4)+  B(8)*B(4)/B(
    35))))/S(I)**2)
     E(I)=-(2.*C+
    1      (A*A*X(I))/(B(2)*B(6) )*(B(9)-B(6)+2.*B(8)*B(6)
    2/B(5))*FAC/S(I)**2   )
     V(I)=(R(I)/S(I))+X(I)*(H(I)+2.*C)
     W(I)=(-A*A*X(I))/(B(2)*B(6)*S(I))+Y(I)*(E(I)+2.*C)
     CONTINUE
     H(999)=H(999)+C
     E(999)=E(999)+C
     P(1)=H(1)
     Q(1)=C/P(1)
     G(1)=V(1)/P(1)
     PP(1)=E(1)
     QQ(1)=C/PP(1)
     GG(1)=W(1)/PP(1)
     DO 4 I=2,999
     P(I)=H(I)-C*Q(I-1)
```

```fortran
      G(I)=(V(I)-C*G(I-1))/P(I)
      PP(I)=E(I)-C*QQ(I-1)
      QQ(I)=C/PP(I)
      GG(I)=(W(I)-C*GG(I-1))/PP(I)
4     CONTINUE
      X(999)=G(999)
      Y(999)=GG(999)
      DO 5 I=1,998
      M=999-I
      X(M)=G(M)-Q(M)*X(M+1)
5     Y(M)=GG(M)-QQ(M)*Y(M+1)
      X1=1000.*X(1)
      Y1=1000.*Y(1)
      IF(ABS(XO-X1)-.001)15,15,16
15    IF(ABS(YO-Y1)-.001)17,17,16
16    XO=X1
      YO=Y1
      IF(ITERAT.GT.25) GO TO 11
      GO TO 7
17    AB=B(4)*X1/(B(4)*X1+B(6)*Y1)
      PRINT 8,A,(B(I),I=1,9),X1,Y1,AB
8     FORMAT(10F6.2,8X,3E16.0)
      GO TO 11
11    STOP
      END
      ENTRY
```

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$JOB      CGG094,TIME008,PAGES030,NAME  J.C.GUPTA   PARALLEL
 $IBJOB
 $IBFTC
          DIMENSION X(1000),Y(1000),H(7000),E(1000),P(1000),Q(1000),S(1000),
         1 PP(1000),QQ(1000),GG(1000),R(1000),S(1000),V(1000),W(1000),B(50)
 C        GENERAL   PROGRAMME   FOR   PARALLEL            REACTIONS   USING
 C             QUASI   LINEARIZATION        TECHNIQUE
 C        FOR   EFFECT   OF   DIFFUSION   AND   ADSORPTION   ON   SELECTIVITY
 C                  OF      SOME      COMPLEX      REAC
  130     FORMAT(/2X,120(1H-))
          C=.1E+07
  11      READ1,A,(B(I),I=1,9)
  1       FORMAT(10F7.2)
          ITERAT=0
          XO=0.
          YO=0.
          DO 2 I=1,1000
          X(I)=.01
  2       Y(I)=.01
          PRINT 130
  7       ITERAT=ITERAT+1
          SS4=B(7)-2.*B(4)+B(8)*F(4)/B(5)
          SS5=B(9)-B(6)+B(8)*B(6)/B(5)
          DY1=A*A/B(2)
          DY2=FAC*(B(9)-B(6)+B(8)*B(6)/B(5))
          AA=-A*A*B(3)/(B(4)*(1.+B(3))           )
          FAC=B(3)/(1.+B(3))
          SS2=2.*SS4*FAC
          DO  3  I=1,999
          R(I)=AA*((1.-2.*B(4)*X(I)-B(6)*Y(I))**2-(B(4)*X(I)/B(5)+B(6)*Y(I)/
         1B(5)) *(X(I)/B(1))           )
          SS1 =(1.+FAC*(SS4*X(I)+Y(I)*SS5))
          RR=-(A*A/(B(2)*B(6)))*(1.-2.*B(4)*X(I)-B(6)*Y(I))
          S(I)=(1.+FAC*(SS4*X(I)+Y(I)*SS5))**2
          DX1=2.*(1.-2.*B(4)*X(I)-B(6)*Y(I))
          DX2=-DX1*2.*B(4)
          DX3=(2.*X(I)*B(4)/B(5)+B(6)*Y(I)/B(5))*(1./B(1))
          H(I)=-(2.*C+(S(I)*AA *(DX2-DX3)-R(I)*SS1*SS2)/S(I)**2   )
          E(I)=-(2.*C+(SS1*DY1-RR *FAC*SS5)/S(I)           )
          V(I)=(R(I)/S(I))+X(I)*(2.*C+H(I))
          W(I)=(RR /SS1)+Y(I)*(2.*C+E(I))
  3       CONTINUE
          H(999)=H(999)+C
```

```
       E(999)=E(999)+C
       P(1)=H(1)
       Q(1)=C/P(1)
       G(1)=V(1)/P(1)
       PP(1)=E(1)
       QQ(1)=C/PP(1)
       GG(1)=W(1)/PP(1)
       DO 4 I=2,999
       P(I)=H(I)-C*Q(I-1)
       Q(I)=C/P(I)
       G(I)=(V(I)-C*G(I-1))/P(I)
       PP(I)=E(I)-C*QQ(I-1)
       QQ(I)=C/PP(I)
   4   GG(I)=(W(I)-C*GG(I-1))/PP(I)
       X(999)=G(999)
       Y(999)=GG(999)
       DO 5 I=1,998
       M=999-I
       X(M)=G(M)-Q(M)*X(M+1)
   5   Y(M)=GG(M)-QQ(M)*Y(M+1)
       X1=X(1)*1000.
       Y1=Y(1)*1000.
       IF(ABS(XO-X1)-.001)15,15,16
  15   IF(ABS(YO-Y1)-.001)17,17,16
  16   XO=X1
       YO=Y1
       IF(ITERAT.GT.25)        GO     TO     11
       GO  TO  7
  17   AB=(1.+B(3)*(1.+2.*B(2)))*B(6)* X1    /(B(2)*B(3)*(2.*B(4)* X1   +B(
      16)*Y1))
       PRINT 8,A,(B(I),I=1,9),X1,Y1,AB
   8   FORMAT(10F6.2,8X,3E16.8)
       GO  TO  11
 111   STOP
       END
$ENTRY
```

APPENDIX B

THIOPHENE HYDROGENOLYSIS: EFFECT OF DIFFUSION LIMITATION ON PRODUCT DISTRIBUTION

B.1 General Reaction Mechanism:

The kinetics of thiophene hydrogenolysis was studied by Roberts [20] over a cobalt molybdate catalyst in a differential reactor with recirculation, the total pressure was about one atmosphere and temperature range 235 - 265 °C. The reaction proceeds as follows:

$$C_4 H_4 S + 3H_2 \longrightarrow C_4 H_8 + H_2 S \qquad (1a)$$

$$C_4 H_8 + H_2 \longrightarrow C_4 H_{10} \qquad (1b)$$
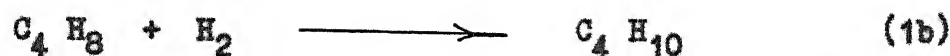
This hydrogenolysis of thiophene is of the form A   B   C. In this case, reaction rate was inhibited by a reaction product, hydrogen sulfide. The rate expression for thiophene disappearance was found to follow [20]:

$$r_T = K \, p_T \, pH \, / \, (1 + K_T \, p_T + K_{H_2S} \, p_{H_2 S})^2 \qquad (2)$$

where r_T is the rate of disappearance of thiophene. p_T, p_H and p_{H_2S} are the partial pressures exerted by thiophene, hydrogen and hydrogen sulphide in mm Hg respectively. K is the reaction rate constant, moles/(gram catalyst)(min)(mm Hg)^2, K_T and K_{H_2S} are the adsorption equilibrium constants for thiophene and H_2S respectively, (mm Hg)$^{-1}$. Both hydrogen sulphide and

thiophene were observed to inhibit the rate of thiophene disappearance significantly. Roberts (20) also established the following butane formation rate based on the assumption that all butene disorbs and re-adsorbs before it is hydrogenated to butane.

$$r_C = \hat{K}\, p_B \;/\; (1 + \hat{K}_B\, p_B + \hat{K}_{H_2S}\, p_{H_2S}) \qquad (3)$$

where K is the reaction rate constant for second reaction, moles/(gram catalyst)(min), (mm Hg), $\hat{K}_B$ and $\hat{K}_{H_2S}$ are adsorption equilibrium constants for butene and H_2S respectively, (mm Hg)$^{-1}$ and p_B is the partial pressure of butene, mm Hg.

The second step in reaction scheme, that is, the hydrogenation of butene to butane, was also found to be retarded by the adsorption of hydrogen sulfide and butene, with butene exerting stronger effect. The fact that denominators of the two rate expressions, equation 2 and 3, are dissimilar suggests that the desulpherization of thiophene and hydrogenation of butene take place on different catalyst sites.

B.2 Mathematical Formulation of the Problem:

For ease of expression we designate C_4H_4S as A, H_2 as B, C_4H_8 as C, H_2S as D and C_4H_{10} as E. Then the reaction becomes

$$A + 3B \longrightarrow C + D$$

$$C + B \longrightarrow E \qquad (4)$$

and the rate expressions for the disappearance of thiophene (A) and the formation of butane (E) can be written as

$$-r_A = K\, p_A\, p_B\, /\, (1 + K_A\, p_A + K_D\, p_D\,)^2 \qquad (5)$$

$$-r_E = \hat{K}\, p_C\, /(1 + \hat{K}_C\, p_C + \hat{K}_D\, p_D) \qquad (6)$$

The rate expressions for other components can be obtained from simple stoichiometry

$$r_C = -\, r_A - r_E \qquad (7a)$$

$$r_D = -\, r_A \qquad (7b)$$

$$-r_B = -3\, r_A + r_E \qquad (7c)$$

Diffusion Inside the Pore:

At steady state, a mass balance of the component diffusing in and out from a small thin shell of thickness dZ at a distance Z from the pore mouth becomes

(Rate of diffusion in the direction of Z at $Z = Z$) (Rate of diffusion in the direction of Z at $Z = Z + dZ$) = Rate of reaction in the shell.

$$-SD_A\left(\frac{dC_A}{dz}\right) - SD_A\left(- \frac{dC_A}{dz} - \frac{d^2C_A}{dz^2}\, dZ \right) = - S\, dz\, r_A \qquad (8)$$

or

$$D_A\, \frac{d^2C_A}{dz^2} = -r_A \qquad (9)$$

where S is the cross sectional area of the pore, C_A is the concentration of component A and D_A is the diffusivity of component A The above equation is valid if transport of material is only due to diffusion and bulk transport due to pressure gradient is

neglected. However, whenever there is change in number of moles/the pressure gradient will exist within the pore. Otani et.al.(19) have studied the effect of pressure gradient on the effect of pressure gradient on the effectiveness of porous catalysts and observed that for small capillaries where Knudson diffusion predominates the influence is insignificant and for a typical bi-disperse catalyst pellet, they concluded that the effect can be important only if the change in moles exceeds two. In general

$$D_i \frac{d^2 C_i}{dz^2} = -r_i \tag{10}$$

where r_i is the rate of formation of component i and negative sign indicates the rate of disappearance. Using the values of r_A, r_C and r_E from equation (10) in equation (7) and assuming ideal gas behaviour, the following partial pressure expressions are obtained after integration and substitution of limits

$$p_C = p_{C_0} + \frac{D_A}{D_C}(p_{A_0}-p_A) + \frac{D_E}{D_C}(p_{E_0}-p_E) \tag{11a}$$

$$p_B = p_{B_0} - \frac{3D_A}{D_B}(p_{A_0}-p_A) + \frac{D_E}{D_B}(p_{E_0}-p_E) \tag{11b}$$

$$p_D = p_{D_0} + \frac{D_A}{D_D}(p_{A_0}-p_A) \tag{11c}$$

When these values are substituted in the rate equations (5)and(6) the following expression results

$$\frac{D_A}{RT}\frac{d^2 p_A}{dz^2} = \frac{K\, p_A\left[p_{B_0}-\frac{3D_A}{D_B}(p_{A_0}-p_A) + \frac{D_E}{D_B}(p_{E_0}-p_E)\right]}{\left[1 + K_A p_A + K_D\left\{p_{D_0} + \frac{D_A}{D_B}(p_{A_0}-p_A)\right\}\right]^2} \tag{12}$$

$$-\frac{D_E}{RT}\frac{d^2 p_E}{dZ^2} = \frac{\hat{K}\left[p_{CO} + \frac{D_A}{D_C}(p_{Ao} - p_A) + \frac{D_E}{D_C}(p_{E_o} - p_E)\right]}{\left[1 + \hat{K}_C\left\{\frac{D_A}{D_C}(p_{Ao} - p_A) + \frac{D_E}{D_C}(p_{E_o} - p_E)\right\} + \hat{K}_D\left\{p_{D_o} + \frac{D_A}{D_D}(p_{Ao} - p_A)\right\}\right]}$$

(13)

These equations can be changed into dimenionless form by defining

$$\emptyset \equiv p/p_o \qquad \eta \equiv Z/L \qquad K_1 \equiv K\, p_o^2$$

$$\frac{K}{K_{p_o}} \equiv K_2 \quad \text{to give}$$

$$\frac{d^2\emptyset_A}{d\eta^2} = +\frac{\emptyset_M^2\emptyset_A\left[\alpha + 3\frac{D_A}{D_B}\emptyset_A - \frac{D_E}{D_B}\emptyset_E\right]}{(1 + K_A p_o)\left[\frac{1}{1 + K_A p_o} + \frac{K_A p_o}{1 + K_A p_o}(\emptyset_A + \gamma - \frac{K_D}{K_A}\frac{D_A}{D_D}\emptyset_A)\right]^2}$$

(14)

where

$$\alpha = \frac{p_{Bo}}{p_o} - \frac{B D_A}{D_B}\frac{p_{Ao}}{p_o} + \frac{D_E}{D_B}\frac{p_{Eo}}{p_o}$$

$$\gamma = \frac{K_D}{K_A}\frac{p_{Do}}{p_o} + \frac{K_D}{K_A}\frac{D_A}{D_D}\frac{p_{Ao}}{p_o}$$

$$\emptyset_M = L\sqrt{\frac{K_1 \, R\, T}{p_o D_A (1 + K_A p_o)}}$$

(15)

and

$$\frac{d^2\emptyset_E}{d\eta^2} = \frac{-K_2\,\emptyset_M^2\left[\xi - \frac{D_A}{D_C}\emptyset_A \frac{D_E}{D_C}\emptyset_E\right]}{\left[\frac{1}{1 + K_A p_o} + \frac{K_C}{K_A}\frac{K_A p_o}{1 + K_A p_o}\left\{\xi - \frac{D_A}{D_C}\emptyset_A - \frac{D_E}{D_C}\emptyset_E\right\} + \frac{\hat{K}_D}{K_A}\frac{K_A p_o}{1 + K_A p_o}\left\{\chi - \frac{D_A}{D_D}\emptyset_A\right\}\right]}$$

(16)

where

$$\xi = \phi_{Co} + \frac{D_A}{D_C} \phi_{Ao} + \frac{D_E}{D_C} \phi_{Eo}$$

$$\chi = \phi_{Do} + \frac{D_A}{D_D} \phi_{Ao} \qquad (17)$$

The equations 14 and 16 are to be solved with the following conditions

$$\phi_A \text{ (at } \eta = 0) = \phi_{Ao}$$

$$\phi_E \text{ (at } \eta = 0) = \phi_{Eo}$$

$$\frac{d\phi_A}{d\eta} \text{ (at } \eta = 1) = \frac{d\phi_E}{d\eta} \text{ (at } \eta = 1) = 0 \qquad (18)$$

The last boundary condition is obtained because no reaction, and hence no diffusion, can take place at the end of the pore. Recognizing that the overall reaction rate with in the pore equals the rate of mass transfer across the pore mouth, the rate of reactions of A and E will be proportional to $D_A \frac{d\phi_A}{d\eta}\Big|_{\eta=0}$ and $D_E \frac{d\phi_E}{d\eta}\Big|_{\eta=0}$ and, therefore selectivity with diffusion effects

$$S_D = \frac{r_C}{-r_A} = \frac{-r_A - r_E}{-r_A} = \frac{\frac{d\phi_A}{d\eta}\Big|_{\eta=0} - \frac{D_E}{D_A} \frac{d\phi_E}{d\eta}\Big|_{\eta=0}}{\frac{d\phi_A}{d\eta}\Big|_{\eta=0}} \qquad (19)$$

The selectivity value can, therefore, be obtained by knowing

$$\left.\frac{d\phi_A}{d\eta}\right|_{\eta=0} \quad \text{and} \quad \left.\frac{d\phi_E}{d\eta}\right|_{\eta=0}$$

The rates of reaction without diffusion effect can simply be written as

$$-r_A = K_1 \phi_A \phi_B / \left[(1 + K_A p_o (\phi_A + \frac{K_D}{K_A} \phi_D))\right]^2 \tag{20}$$

$$-r_E = K_1 K_2 \phi_C / \left[1 + K_A p_o (\phi_C \frac{K_C}{K_A} + \phi_D \frac{K_D}{K_A})\right] \tag{21}$$

Hence selectivity without diffusion effects

$$S_o = 1 - \frac{\phi_C K_2 \left[1 + K_A p_o (\phi_A + \frac{K_D}{K_A} \phi_D)\right]^2}{\left[1 + K_A p_o (\phi_C \frac{K_C}{K_A} + \phi_D \frac{K_D}{K_A})\right] \phi_A \phi_B} \tag{21}$$

B-3: Product Distribution and Selectivity with Conversion:

The computation was carried out by taking the initial partial pressures of reactants A and B as 0.1 and 0.9 respectively and the selectivity calculated for any given value of modified Thiele parameter using this value of selectivity and taking a constant increment 0.001 (one percent of the initial partial pressure of A) change in the value of partial pressure of A the product distribution for next step was calculated.

If $\triangle$ is the change in the partial pressure of A and S_{D_o} the selectivity, then the new values of the partial pressures

of B, C, D and E can be calculated from the following stoichiometric relations

$$A_1 = A_0 - \triangle$$
$$B_1 = B_0 - (3 \times S_{D_0} + 4(1 - S_{D_0}))\triangle$$
$$C_1 = C_0 + S_{D_0} \times \triangle$$
$$D_1 = D_0 + \triangle$$
$$E_1 = E_0 + (1 - S_{D_0})\triangle \qquad (22)$$

Due to changes in the number of moles of the reactants and products, the partial pressure of each component was normalized by dividing the individual partial pressure by sum of the partial pressures of all components. These normalized values of partial pressures were then used to calculate the new value of selectivity, S_{D_1}. The values of partial pressures for next step were calculated from equation (22) by changing the numerical subscripts, that is, writing 2 in place of 1 and 1 in place of o. The procedure was repeated upto any desired conversion. Computations were made for modified Thiele parameter values of 0.2, 0.5, 1.0, 1.5 and 2.0 and thiophene conversion of 0 to 100 percent.

For the study of selectivity without any diffusion limitation, the selectivity was found to be very sensitive to the changes in the partial pressure values. An iterative technique was, therefore, used to obtain the truly representative average value of selectivity for any incremental change in the

partial pressure of A. In the iteration procedure, selectivity S_0 was computed for partial pressure values of A_0, B_0, C_0, D_0 and E_0. For incremental change $\triangle$ as a first approximation the new values of A_{11}, B_{11}, C_{11}, D_{11} and E_{11} were computed from equation (22) by replacing S_0 in place of S_{D_0}. New selectivity value S_{11} was then computed from partial pressure values of A_{11} to E_{11}. The improved value of selectivity that is $(S_0 + S_{11})/2$, was taken and with this, new values of A_{12}, B_{12}, C_{12}, D_{12} and E_{12} were computed from equation (22). New selectivity value was then computed from partial pressures A_{12} to E_{12}. This procedure was continued till the difference of $(n-1)^{th}$ and n^{th} selectivity was less than 0.0001. This iterative technique was used to calculate the values of selectivity, S_0, for 0 to 100 percent conversion of thiophene.

B-4: Results and Discussions:

For any given system, only the modified Thiele parameter, ϕ_M can be varied independently by varying catalyst pellet size. All other dimensionless variables involving diffusion, adsorption or reaction rate constant assume constant values. Robert(20) gave the following values for the constants at 250°C.

$$K(\text{moles/gram catalyst, min., mm Hg}^2) = 0.178 \times 10^{-8}$$

$$K_A(\text{mm Hg}^{-1}) = 0.0284$$

$$K_D(\text{mm Hg}^{-1}) = 0.0237$$

$$K(\text{moles/gram catalyst, min, mm Hg}) = 0.269 \times 10^{-5}$$

$$K_C(\text{mm Hg}^{-1}) = 0.463$$

$$K_D(\text{mm Hg}^{-1}) = 0.0884$$

where K is reaction rate constant, K_A and K_D are adsorption equilibrium constants for the first step of the reaction. K is the reaction rate constant, K_C and K_D are adsorption equilibrium constants for the second step of the reaction. A, B, C, D and E are representing thiophene, hydrogen, butene, hydrogen sulfide and butane respectively. These constants were changed to the following dimensionless variables and then used for the calculation of the selectivity.

$$K_1 \equiv K \, p_o^2$$
$$K_2 \equiv K_1/K \, p_o$$
$$K_A p_o$$

Ratio of diffusivities, D_B/D_A, D_C/D_A, D_D/D_A and D_E/D_A
Ratio of adsorption equilibrium constants K_D/K_A, K_C/K_A, K_D/K_A

The values of effective diffusivities of components B, C, D and E were calculated using the method as described by Robert[20] while calculating the effective diffusivity of thiophene. The values of binary diffusion coefficients (for diffusion in hydrogen) and Knudsen diffusion coefficient were calculated using the relationships given by Sherwood and Satterfield [2]. The results presented in Tables 9 to 14 show the percent thiophene converted, normalized values of partial pressures of component A, B, C, D and E, ratio of C to E, percent conversion to C, for different values of modified Thiele parameter in the range of 0.2 to 2.0 as well as for a case when no diffusion limitation exists.

The value of selectivity when diffusion limitations does not exist as given in Table 9 page 54 indicate that these are very sensitive to the composition and decreases rapidly as conversion of thiophene to butene or butane increases. The selectivity value changes from unity at zero percent thiophene conversion to a minimum value nearly -1.145 at conversion level of approximately 92 percent. As the conversion level increases further the selectivity value also increases and attains a value of approximately - 0.477 at 100 percent conversion. Percent conversion to butene increases with increase in thiophene conversion upto a conversion level of 64 percent and then it is found to decrease with further increase in conversion of thiophene. The maximum butene conversion is found to be 23.74 percent at a thiophene conversion of 60 percent. The ratio of butene to butane in product decreases from infinity to zero as the thiophene conversion increases from zero to 100 percent. These observations are in conformity with those obtained for simple series reaction(25)

The following are some of the observations made on analysing the results presented in tables 10 to 14 and figure 2 with diffusion limitations:

(i) The values of selectivity when diffusion limitations exist were less at higher values of modified Thiele parameter than at lower values of Thiele parameter. Thus the partial pressure of butene was less at higher values of Thiele parameter than at lower values of Thiele parameter.

(ii) The ratio of butene to butane in product decreased with the increase in conversion at lower values of modified Thiele parameter i.e. at 0.2 and 0.5, but was almost constant at higher values of modified Thiele parameter, i.e. at 1.5 and 2. In this study, with diffusion limitations, the ratio of butene to butane in product attains a constant value of 0.53 at 100 percent conversion of thiophene. These observations were not in conformity with the results obtained when no diffusion limitations exist. The expected behaviour of the results in Fig. 2 and tables 10 to 14 with diffusion limitations is that, they should be always below the result for without diffusion limitation. The reason for this doubtful behaviour may be the approximate results obtained with invariant imbedding technique. This approximation of the results will be multiplied as the thiophene conversion will proceed to 100 percent with $\triangle$ increment for each step of conversion and hence this may be the reason of 34 percent of butene at 100 percent thiophene conversion.

TABLE 9: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR NO DIFFUSION LIMITATION

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	1.0
4.98	0.096	0.894	0.004	0.005	0.001	3.99	3.98	0.7
9.90	0.092	0.888	0.007	0.010	0.003	2.51	7.08	0.595
15.73	0.088	0.880	0.011	0.016	0.006	1.91	10.32	0.531
20.52	0.084	0.873	0.013	0.022	0.008	1.64	12.74	0.488
25.25	0.080	0.867	0.016	0.027	0.010	1.45	14.94	0.448
29.92	0.076	0.860	0.018	0.032	0.014	1.30	16.90	0.407
35.45	0.071	0.852	0.021	0.039	0.018	1.15	18.99	0.354
39.99	0.067	0.845	0.023	0.044	0.022	1.05	20.47	0.306
45.36	0.062	0.836	0.025	0.051	0.027	0.935	21.98	0.242
50.63	0.057	0.827	0.026	0.058	0.032	0.831	22.97	0.169
54.97	0.052	0.819	0.027	0.064	0.037	0.748	23.55	0.098
60.08	0.047	0.810	0.028	0.071	0.043	0.654	23.74	0.0006
65.10	0.042	0.800	0.028	0.079	0.050	0.562	23.42	-0.116
70.03	0.037	0.791	0.028	0.086	0.059	0.472	22.46	-0.256
75.66	0.031	0.779	0.026	0.095	0.070	0.369	20.39	-0.456
80.38	0.025	0.768	0.023	0.104	0.081	0.282	17.68	-0.664
85.00	0.020	0.756	0.018	0.112	0.094	0.197	13.99	-0.900
90.25	0.013	0.742	0.012	0.122	0.111	0.104	8.53	-1.127
95.35	0.007	0.728	0.004	0.133	0.129	0.032	2.98	-0.960
99.61	0.001	0.715	0.000	0.142	0.142	0.002	0.195	-0.477

TABLE 10: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR β_M = 0.2

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	–	0.0	0.754
4.98	0.096	0.894	0.004	0.005	0.002	2.31	3.47	0.639
9.90	0.092	0.887	0.007	0.010	0.004	1.92	6.50	0.585
14.76	0.088	0.881	0.010	0.015	0.006	1.69	9.27	0.549
20.50	0.084	0.875	0.013	0.022	0.009	1.52	12.36	0.516
25.24	0.080	0.867	0.016	0.027	0.011	1.41	14.75	0.491
29.91	0.076	0.859	0.018	0.032	0.014	1.32	17.00	0.467
35.44	0.071	0.852	0.021	0.039	0.017	1.23	19.52	0.439
39.99	0.067	0.845	0.024	0.044	0.021	1.16	21.47	0.414
45.36	0.062	0.836	0.027	0.051	0.024	1.09	23.63	0.384
50.65	0.056	0.828	0.029	0.058	0.029	1.02	25.58	0.350
55.86	0.051	0.819	0.032	0.065	0.053	0.958	27.33	0.314
60.13	0.057	0.811	0.034	0.071	0.057	0.910	28.62	0.282
65.18	0.042	0.802	0.036	0.078	0.042	0.850	29.96	0.240
70.16	0.036	0.795	0.038	0.085	0.048	0.795	31.06	0.197
75.05	0.031	0.783	0.040	0.093	0.053	0.740	31.94	0.153
80.65	0.024	0.772	0.041	0.102	0.061	0.681	32.67	0.106
85.36	0.019	0.761	0.043	0.110	0.067	0.634	33.15	0.080
89.99	0.013	0.751	0.044	0.118	0.074	0.592	33.47	0.079
95.28	0.006	0.739	0.045	0.127	0.082	0.554	33.96	0.116
99.74	0.000	0.728	0.047	0.136	0.089	0.530	34.55	0.104

TABLE 17: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR $\phi_M = 0.5$

% A con-verted	A	B	C	D	E	Ratio C/E	% conver-ted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.557
4.98	0.096	0.894	0.003	0.005	0.002	1.2	2.71	0.530
9.89	0.092	0.887	0.006	0.010	0.005	1.14	5.27	0.509
15.71	0.088	0.880	0.009	0.016	0.008	1.09	8.18	0.487
20.49	0.084	0.873	0.011	0.022	0.011	1.05	10.47	0.470
25.00	0.080	0.866	0.014	0.027	0.013	1.01	12.16	0.452
30.80	0.075	0.858	0.016	0.033	0.017	0.976	15.13	0.431
35.39	0.071	0.851	0.019	0.039	0.020	0.933	17.08	0.413
40.82	0.066	0.843	0.021	0.046	0.024	0.895	19.27	0.391
45.28	0.062	0.836	0.023	0.051	0.027	0.864	20.98	0.381
50.55	0.057	0.827	0.026	0.058	0.032	0.827	22.89	0.347
55.75	0.052	0.818	0.029	0.065	0.036	0.792	24.64	0.321
60.00	0.047	0.811	0.031	0.071	0.040	0.763	25.97	0.299
65.05	0.042	0.802	0.033	0.078	0.045	0.729	27.42	0.272
70.01	0.037	0.792	0.035	0.086	0.050	0.695	28.71	0.245
75.03	0.030	0.782	0.037	0.094	0.057	0.658	30.05	0.215
80.48	0.025	0.771	0.039	0.102	0.063	0.627	31.01	0.194
85.18	0.019	0.761	0.041	0.110	0.069	0.598	31.89	0.179
90.57	0.012	0.750	0.043	0.119	0.076	0.569	32.84	0.174
95.10	0.007	0.739	0.045	0.127	0.082	0.547	33.64	0.184
99.56	0.001	0.729	0.047	0.135	0.088	0.530	34.50	0.204

TABLE 19: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY FOR $\alpha_M = 1.0$

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	—	0.0	0.400
4.97	0.096	0.894	0.002	0.005	0.003	0.663	1.98	0.396
9.88	0.092	0.887	0.004	0.010	0.006	0.656	3.92	0.391
15.69	0.088	0.879	0.006	0.016	0.010	0.649	6.18	0.386
20.46	0.084	0.873	0.009	0.022	0.013	0.643	8.00	0.381
25.17	0.080	0.866	0.011	0.027	0.017	0.636	9.79	0.376
30.74	0.075	0.858	0.013	0.033	0.021	0.629	11.87	0.369
35.31	0.071	0.851	0.015	0.039	0.024	0.622	13.54	0.364
40.70	0.066	0.842	0.017	0.046	0.028	0.614	15.50	0.357
45.17	0.062	0.835	0.019	0.051	0.032	0.608	17.08	0.352
50.42	0.057	0.827	0.022	0.058	0.036	0.600	18.90	0.345
55.59	0.052	0.818	0.024	0.065	0.041	0.592	20.68	0.339
60.68	0.047	0.809	0.027	0.072	0.046	0.585	22.39	0.332
65.69	0.042	0.800	0.029	0.079	0.050	0.578	24.05	0.326
70.62	0.036	0.790	0.032	0.087	0.055	0.570	25.64	0.320
75.47	0.031	0.781	0.034	0.094	0.060	0.563	27.18	0.314
80.24	0.025	0.771	0.036	0.102	0.065	0.556	28.67	0.309
85.71	0.019	0.760	0.039	0.111	0.072	0.548	30.34	0.303
90.32	0.013	0.750	0.042	0.119	0.077	0.542	31.73	0.298
95.60	0.006	0.738	0.045	0.128	0.083	0.534	33.30	0.294
99.30	0.001	0.729	0.047	0.135	0.088	0.530	34.39	0.294

TABLE II: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY AT $\phi_M = 1.5$

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.325
4.97	0.096	0.894	0.002	0.005	0.003	0.488	1.63	0.332
9.88	0.093	0.887	0.003	0.010	0.007	0.495	3.27	0.337
15.68	0.088	0.879	0.006	0.016	0.011	0.502	5.24	0.343
20.45	0.084	0.873	0.007	0.022	0.014	0.507	6.88	0.347
25.15	0.080	0.866	0.009	0.027	0.018	0.513	8.52	0.350
30.71	0.095	0.858	0.011	0.033	0.022	0.518	10.48	0.353
35.28	0.071	0.851	0.013	0.039	0.026	0.522	12.10	0.355
40.68	0.067	0.842	0.016	0.046	0.030	0.526	14.02	0.356
45.12	0.062	0.835	0.018	0.051	0.034	0.528	15.60	0.357
50.36	0.057	0.826	0.020	0.058	0.038	0.531	17.47	0.356
55.53	0.052	0.818	0.023	0.065	0.043	0.533	19.31	0.355
60.61	0.047	0.809	0.025	0.072	0.047	0.535	21.10	0.354
65.61	0.042	0.800	0.028	0.079	0.052	0.535	22.88	0.351
70.54	0.036	0.790	0.030	0.087	0.057	0.536	24.60	0.349
75.38	0.031	0.781	0.033	0.094	0.061	0.535	26.28	0.346
80.15	0.025	0.771	0.036	0.102	0.066	0.535	27.92	0.342
85.62	0.019	0.760	0.039	0.111	0.072	0.534	29.50	0.339
90.23	0.013	0.750	0.041	0.119	0.077	0.532	31.34	0.336
95.51	0.006	0.738	0.044	0.128	0.084	0.531	33.10	0.332
99.96	0.000	0.728	0.047	0.136	0.089	0.529	34.57	0.323

TABLE 14: DATA FOR PRODUCT DISTRIBUTION AND SELECTIVITY AT $\theta_M = 2.0$

% A converted	A	B	C	D	E	Ratio C/E	% converted to C	S_D
0.0	0.1	0.9	0.0	0.0	0.0	-	0.0	0.325
4.97	0.096	0.894	0.002	0.005	0.005	0.483	1.62	0.326
9.88	0.093	0.887	0.003	0.010	0.007	0.483	3.22	0.326
15.68	0.088	0.879	0.005	0.016	0.011	0.484	5.10	0.327
20.45	0.084	0.873	0.007	0.022	0.015	0.484	6.67	0.327
25.15	0.090	0.866	0.009	0.027	0.018	0.485	8.21	0.329
30.71	0.076	0.858	0.011	0.033	0.023	0.486	10.04	0.332
35.27	0.072	0.851	0.013	0.039	0.026	0.488	11.56	0.335
40.67	0.067	0.842	0.015	0.046	0.031	0.490	13.38	0.340
45.10	0.062	0.835	0.017	0.051	0.034	0.493	14.90	0.345
50.35	0.058	0.826	0.019	0.058	0.039	0.498	16.72	0.353
55.50	0.052	0.818	0.022	0.065	0.043	0.503	18.56	0.360
60.59	0.047	0.809	0.024	0.072	0.048	0.508	20.41	0.367
65.59	0.042	0.799	0.027	0.079	0.053	0.514	22.26	0.373
70.51	0.036	0.790	0.030	0.087	0.057	0.519	24.10	0.376
75.35	0.031	0.781	0.032	0.094	0.062	0.524	25.92	0.375
80.12	0.025	0.771	0.035	0.102	0.067	0.528	27.70	0.370
85.59	0.019	0.760	0.038	0.111	0.072	0.531	29.69	0.358
90.19	0.013	0.750	0.041	0.119	0.077	0.532	31.32	0.344
95.48	0.006	0.738	0.044	0.128	0.084	0.531	33.10	0.330
99.93	0.000	0.728	0.047	0.136	0.089	0.529	34.56	0.344
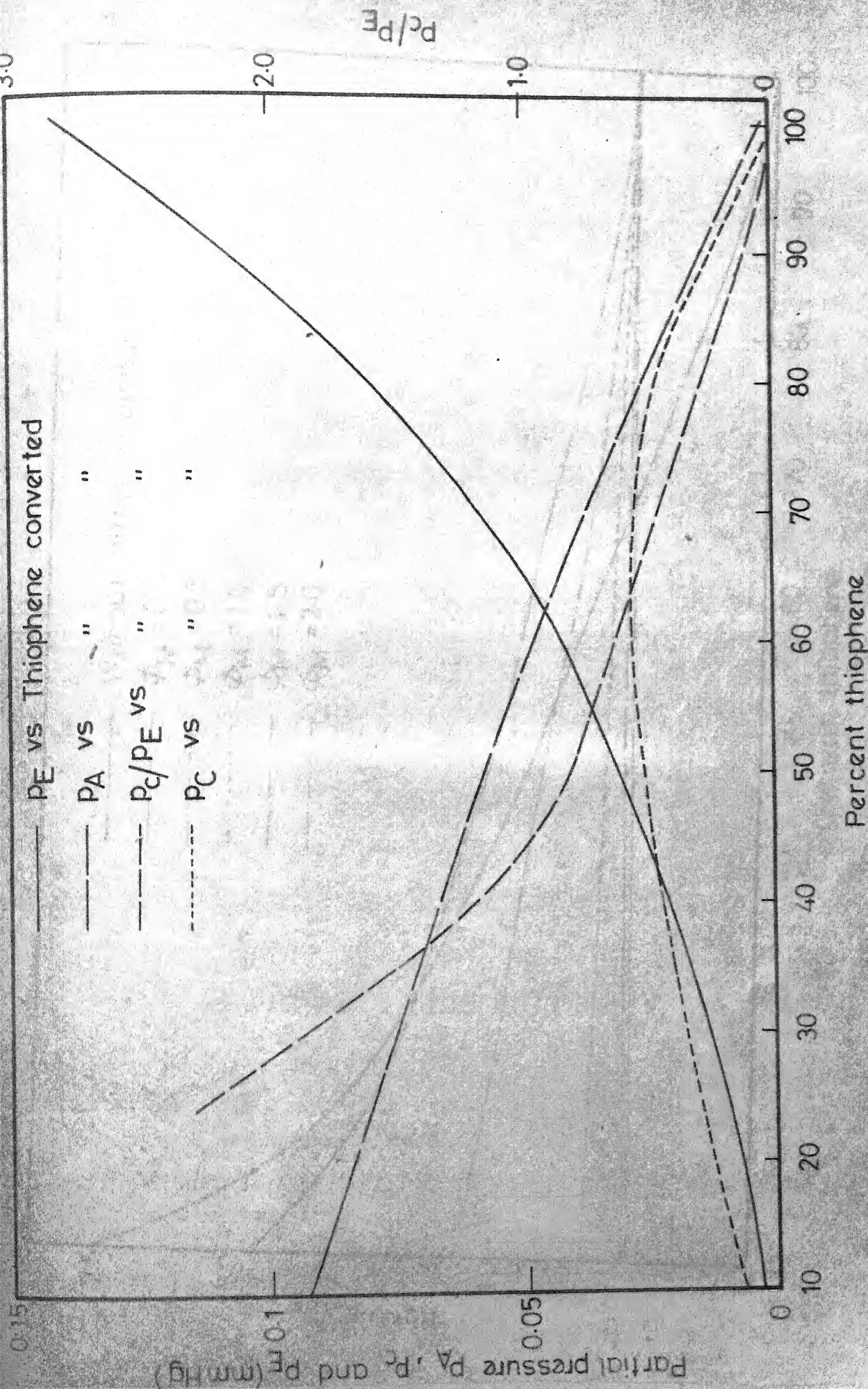
Fig.1 - Partial pressure of thiophene, p_A, Butene, p_C, Butane, p_E and ratio of Butene to Butane, p_C/p_E as a function of percent Thiophene converted.

p_E vs Thiophene converted
p_A vs " "
p_C/p_E vs " "
p_C vs " "

Percent thiophene

Partial pressure p_A, p_C and p_E (mmHg)
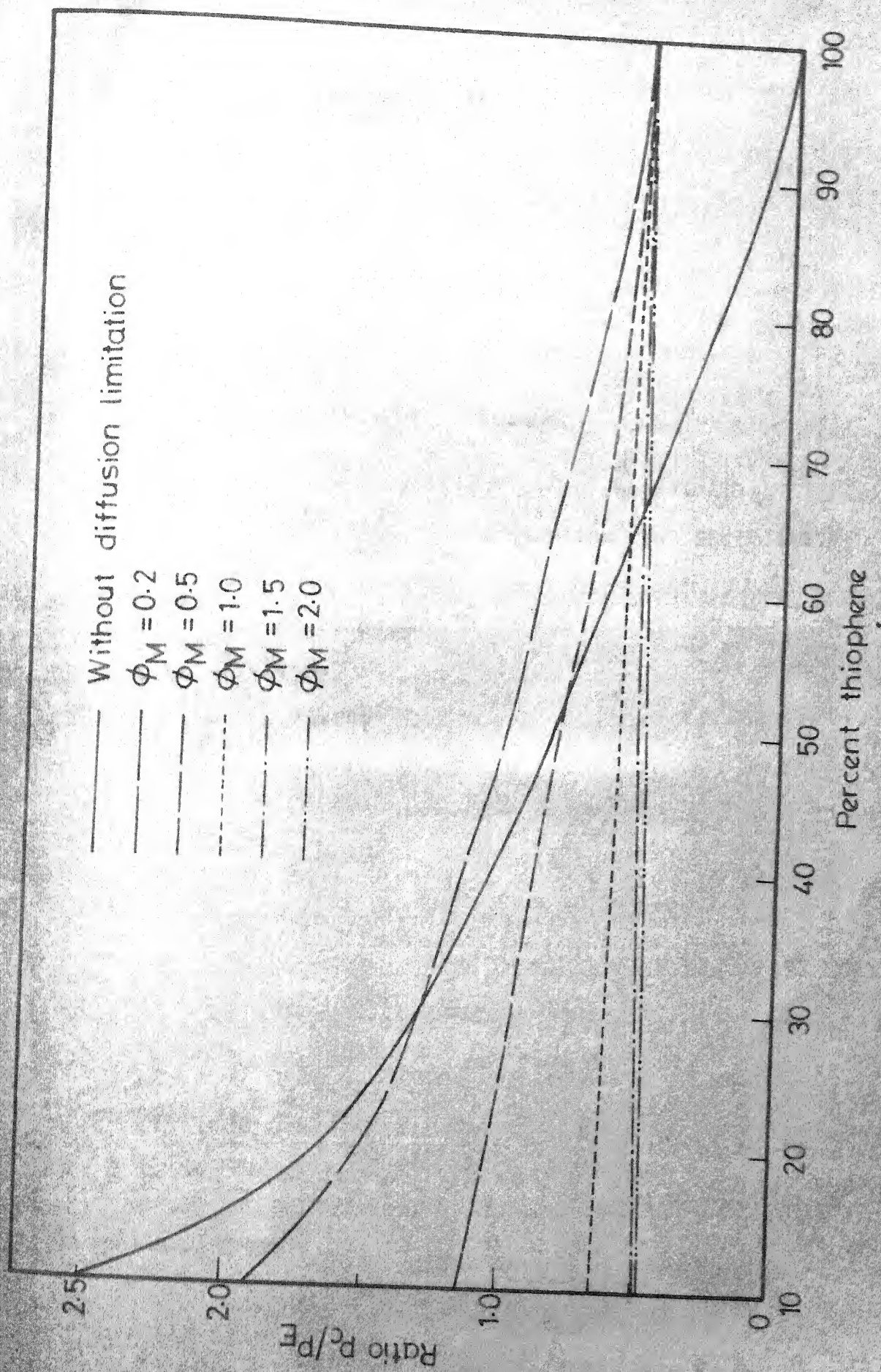
p_C/p_E

Fig 2—Ratio of butene to butane, P_C/P_E, as a function of percent thiophene converted for selected values of modified Thiele parameter, ϕ_M, and without diffusion limitation.

```
  CGG094,TIME030,PAGES035,NAME    J.C.GUPTA
B
C
  DIMENSION  U(4,4),V(4,4),W(4,4),X(3),AA(2),BB(2),CC(2)
  GENERAL PROGRAMME FOR SERIES  REACTIONS
  FOR  EFFECT  OF  DIFFUSION  AND  ADSORPTION  ON  SELECTIVITY
  RATIO USING COMPLEX  REACTIONS
  READ 61,((U(K,L),L=1,3),K=1,3)
  FORMAT(3F15.8)
  EQUIVALENCE   (CC,AML),(DO,EML)
  COMMON  A,B(20)
  READ51,A,(B(I),I=1,10)
  FORMAT(11F7.4)
  PRINT  69,A,(B(I),I=1,10)
  FORMAT(10X,11F9.4)
  VV=1.
  PP=.1
  QQ=.9
  GG=0.
  HH=0.
  WW=0.
  DEL=.001
  E1ML=0.0
  EOML=0.
  EML=0.
  C1ML=-.001
  CML=-.001
  COML=-.001
  D1ML=-.001
  DML=-.001
  DOML=-.001
  AML=.101
  A1ML=.101
  AOML=.101
  B1ML=.903
  BOML=.903
  BML=.903
  MM=0
  UU=1.
  DO  100   IK=1,120
```

```
A1ML=A1ML-DEL
C1ML=C1ML+DEL*VV
D1ML=D1ML+DEL
E1ML=E1ML+DEL*(1.-VV)
B1ML=B1ML-(3.*VV+4.*(1.-VV))*DEL
AOML=AOML-DEL
COML=COML+DEL*UU
DOML=DOML+DEL
EOML=EOML+(1.-UU)*DEL
BOML=BOML-(3.*UU+4.*(1.-UU))*DEL
AML=AML-DEL
CML=CML+DEL*VV
DML=DML+DEL
EML=EML+(1.-VV)*DEL
BML=BML-(3.*VV+4.*(1.-VV))*DEL
IF(EML)501,500,501
GML=0.
GO TO 505
GML=CML/EML
M=0
IF(EOML)511,521,511
GOML=0.
GO TO 506
GOML=COML/EOML
M=0
SIGMA=AML+BML+CML+DML+EML
AML=AML/SIGMA
BML=BML/SIGMA
CML=CML/SIGMA
DML=DML/SIGMA
EML=EML/SIGMA
APCN=(1.-AML/(AML+CML+EML))*100.
CPCN=(CML/(AML+CML+EML))*100.
PRINT 333,AML,BML,CML,DML,EML,GML       ,APCN,CPCN
3 FORMAT(10X,8F12.6)
WSIGMA=AOML+BOML+COML+DOML+EOML
AOML=AOML/WSIGMA
BOML=BOML/WSIGMA
COML=COML/WSIGMA
DOML=DOML/WSIGMA
EOML=EOML/WSIGMA
PRINT 555,AOML,BOML,COML,DOML,EOML,GOML
5 FORMAT(6F12.6)
DO 99 J=8,10
N=0
N1=0
N2=0
N3=0
N4=0
N5=0
R=J
Q=1./R
P=Q*Q
C=CO
D=DO
```

```fortran
5     N=N+1
      C1=C-P*F(C,D)
      D1=D-P*G(C,D)
      C2=C1-P*F(C1,D1)
      D2=D1-P*G(C1,D1)
      C1=C2-P*F(C2,D2)
      D1=D2-P*G(C2,D2)
      GO TO(7,28,7,29,7,1,7,12,7,3,7,3,7,1,7,14,7,6,7,6,7,1,7,6,7,3,7,3,
     1 7,1,7,21,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
     2 7,1,7,19,7,4,7,4,7,1,7,4,7,3,7,3,7,1,7,8,7,6,7,6,7,1,7,6,7,3,7,3,
     3  7,1,7,4,7,8,7,8,7,1,7,8,7,3,7,3,7,1,7,4,7,6,7,6,7,1,7,6,7,3,7,3,
     4  7,1,7,25),N
7     C3=C-P*(F(C,D)+F(C1,D1)+F(C2,D2))
      D3=D-P*(G(C,D)+G(C1,D1)+G(C2,D2))
      C=C3
      D=D3
      GO TO 5
28    C=C0
      D=D0
11    C4=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3))
      D4=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3))
      C=C4
      D=D4
      GO TO 5
29    C=C0
      D=D0
15    C5=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4))
      D5=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4))
1     C=C5
      D=D5
      N1=N1+1
      GO TO(5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11,
     1       5,11,5,11,5,11,5,11,5,11,5,11,5,11,5,11),N1
12    C=C0
      D=D0
20    C6=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5))
      D6=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5))
3     C=C6
      D=D6
      N2=N2+1
      GO TO(5,11,15,5,11,15,5,11,15,5,11,15,
     1       5,11,15,5,11,15,5,11,15,5,11,15),N2
14    C=C0
      D=D0
18    C7=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
     1F(C6,D6))
      D7=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
     1 G(C6,D6))
6     C=C7
      D=D7
      N3=N3+1
      GO TO(5,11,15,20,5,11,15,20,5,11,15,20,5,11,15,20),N3
```

```fortran
21   C=C0
     D=D0
22   C8=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(+C5,D5)+
    1 F(C6,D6)+F(C7,D7))
     D8=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
    1 G(C6,D6)+G(C7,D7))
     IF(J-8)8,40,8
40   V(1,4)=(C8-C0)/Q
     W(1,4)=(D8-D0)/Q
     GO TO 99
8    C=C8
     D=D8
     N4=N4+1
     GO  TO(5,11,15,20,18,5,11,15,20,18),N4
19   C=C0
     D=D0
     C9=C-P*(F(C,D)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
    1 F(C6,D6)+F(C7,D7)+F(C8,D8))
     D9=D-P*(G(C,D)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
    1 G(C6,D6)+G(C7,D7)+G(C8,D8))
     IF(J-9)4,41,4
41   V(2,4)=(C9-C0)/Q
     W(2,4)=(D9-D0)/Q
     GO TO 99
4    C=C9
     D=D9
     N5=N5+1
     GO TO(5,11,15,20,18,22),N5
     C10=C0-P*(F(C0,D0)+F(C1,D1)+F(C2,D2)+F(C3,D3)+F(C4,D4)+F(C5,D5)+
    1F(C6,D6)+F(C7,D7)+F(C8,D8)+F(C9,D9))
     D10=D0-P*(G(C0,D0)+G(C1,D1)+G(C2,D2)+G(C3,D3)+G(C4,D4)+G(C5,D5)+
    1 G(C6,D6)+G(C7,D7)+G(C8,D8)+G(C9,D9))
     V(3,4)=(C10-C0)/Q
     W(3,4)=(D10-D0)/Q
99   CONTINUE
68   DO 62 K=1,3
     DO 62 L=1,3
62   V(K,L)=U(K,L)
     DO 63 I=1,2
     II=I+1
     DO 63 K=II,3
     DO 63 L=II,4
63   V(K,L)=V(K,L)-V(I,L)*V(K,I)/V(I,I)
     DO 64 LQ=3,4
     LL=6-LQ
     LJ=LL-1
     DO 64 K=1,LJ
64   V(K,4)=V(K,4)-V(LL,4)*V(K,LL)/V(LL,LL)
     DO 65 K=1,3
65   X(K)=V(K,4)/V(K,K)
     DO 67 K=1,3
67   V(K,4)=W(K,4)
     M=M+1
     AA(M)=X(1)
     BB(M)=X(2)
     CC(M)=X(3)
     IF(M-2)68,98,98
```

```
 98    UU=1.-(B(1)*B(2)*COML*(1.+B(3)*(AOML+B(8)*DOML))**2)
      1/((1.+B(3)*(COML*B(9)+DOML*B(10)))*B(1)*AOML*BOML)
       VV=1.+B(7)*AA(2)/AA(1)
       AB=VV/UU
       PRINT  71,AA(1),AA(2),BB(1),CC(1),BB(2),CC(2)        ,VV,UU,AB
 71    FORMAT(9F12.6)
       IF(B1ML)222,444,444
 222   GO  TO  2
 444   CONTINUE
       PRINT  130
 130   FORMAT(/2X,120(1H-))
 100   CONTINUE
       GO   TO  2
  97   STOP
       END
$IBFTC FUN1
       FUNCTION F(C,D)
       COMMON  A,B(20)
       WW=0.
       HH=0.
       PP=.1
       QQ=.9
       GG=0.
       BB113=1./(1.+B(3))
       BB313=B(3)*BB113
       GAMA=B(8)*(HH+PP/B(6))
       ALPHA=QQ-3.*PP/B(4)+B(7)*WW/B(4)
       R=(A*A*C*(ALPHA+3.*C /B(4)-D*B(7)/B(4)))
       S=(1.+B(3))*(BB113+BB313*(C+GAMA-B(8)*C/B(6)))**2
       F=R/S
       RETURN
       END
$IBFTC FUN2
       FUNCTION G(C,D)
       COMMON  A,B(20)
       WW=0.
       HH=0.
       PP=.1
       QQ=.9
       GG=0.
       BB113=1./(1.+B(3))
       BB313=B(3)*BB113
       ZEE=GG+PP/B(5)+B(7)*WW/B(5)
       SIE=HH+PP/B(6)
       SS=     (BB113+BB313*B(9)*(ZEE-C     /B(5)-B(7)*D/B(5))+BB313*B(10)
       R1=-A*A*B(2)*(ZEE-C      /B(5)-D*B(7)/B(5))
      1*(SIE-C      /B(6)))
       G=R1/SS
       RETURN
       END
$ENTRY
    1.               .125               .015625
    1.               .11111111          .01234568
    1.               .1                 .01
```